NUCLEATION OF TERRESTRIAL BIOGENIC/ANTHROPOGENIC AEROSOLS

Robert McGraw[1] and Renyi Zhang[2]

- *An application of the "nucleation theorem"*

$$J = \sum_i J_i = \sum_i \kappa_i \beta_i n(g*_1, g*_2, L)$$

Transition state model

critical cluster population

$$\left(\frac{\partial \ln J}{\partial \ln n_i} \right)_{T,\{n_j, j \neq i\}} = g*_i + \delta_i$$

N-theorem
essentially law of mass action

$$\ln J \approx \ln J_0 + \sum_i (g*_i + \delta_i)(\ln n_i - \ln n_i^0)$$
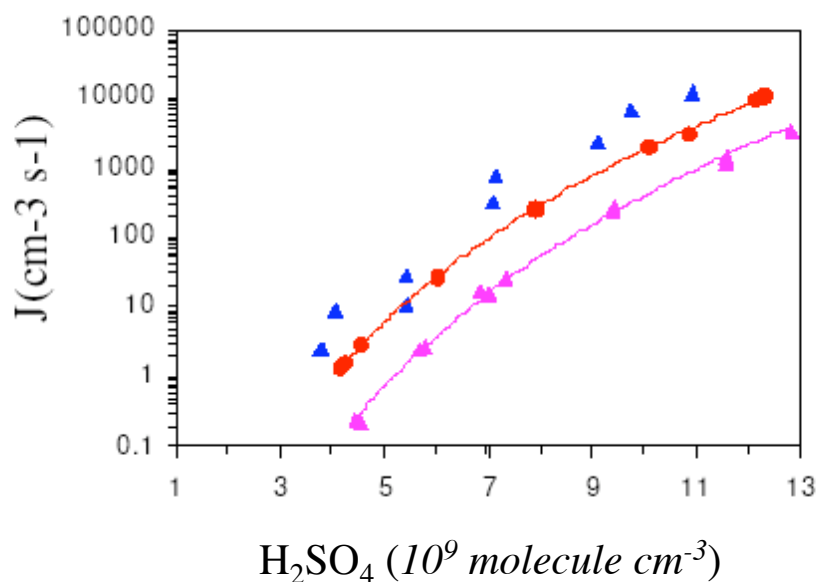
small kinetic term (0 < δ_i < 1)

nucleus content species i

Atmospheric New Particle Formation Enhanced by Organic Acids

Renyi Zhang,[1]* Inseon Suh,[1] Jun Zhao,[1] Dan Zhang,[1] Edward C. Fortner,[1] Xuexi Tie,[2] Luisa T. Molina,[3] Mario J. Molina[3]

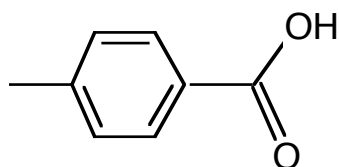- Nucleation in the ternary p-toluic acid/sulfuric acid/water systems

Red circle – 0.2 ppb p-toluic acid
Blue triangle – 0.4 ppb p-toluic aicd
Pink triangle - no p-toluic acid
RH = 5%

- These are systems *not* amenable to analysis using CNT.
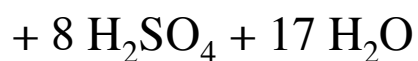
- How to make progress?

(critical nucleus composition from measurements of Zhang et al., Science, 2004)

$+ 8 H_2SO_4 + 17 H_2O$ $\Longleftrightarrow$ critical nucleus $\xrightarrow{growth}$ laboratory NPF
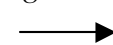
p-toluic acid

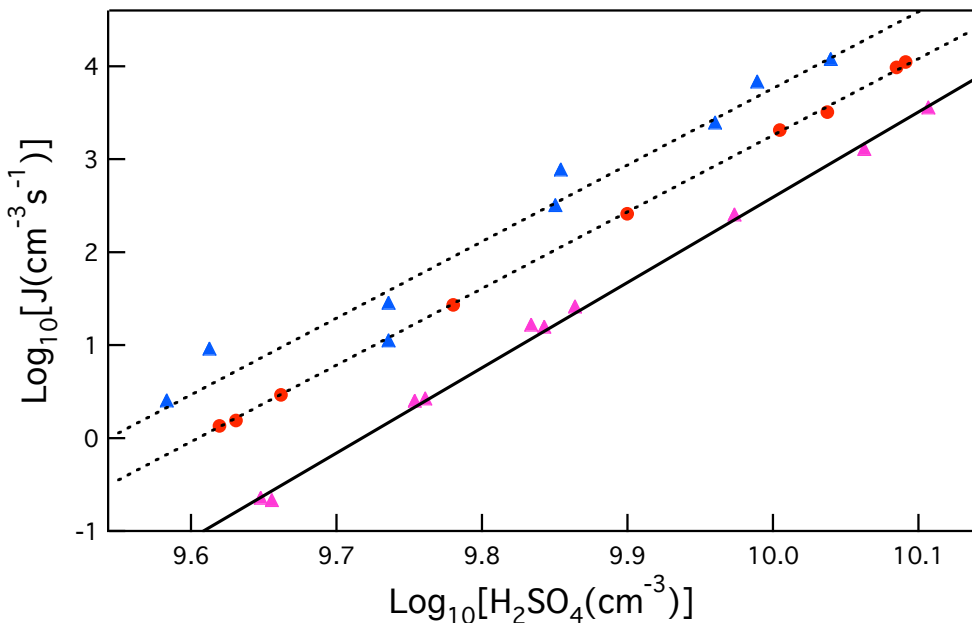**Laboratory chamber measurements:**

Theory: "nucleation theorem" + multi-linear data analysis yields nucleus molecular content

Red circle – 0.2 ppb p-toluic acid
Blue triangle – 0.4 ppb p-toluic aicd
Pink triangle - no p-toluic acid
RH = 5%

R. McGraw and R. Zhang, Multivariate analysis of homogeneous nucleation rate measurements: Nucleation in the p-toluic acid/sulfuric acid/water system, JCP 128, 064508 (2008).

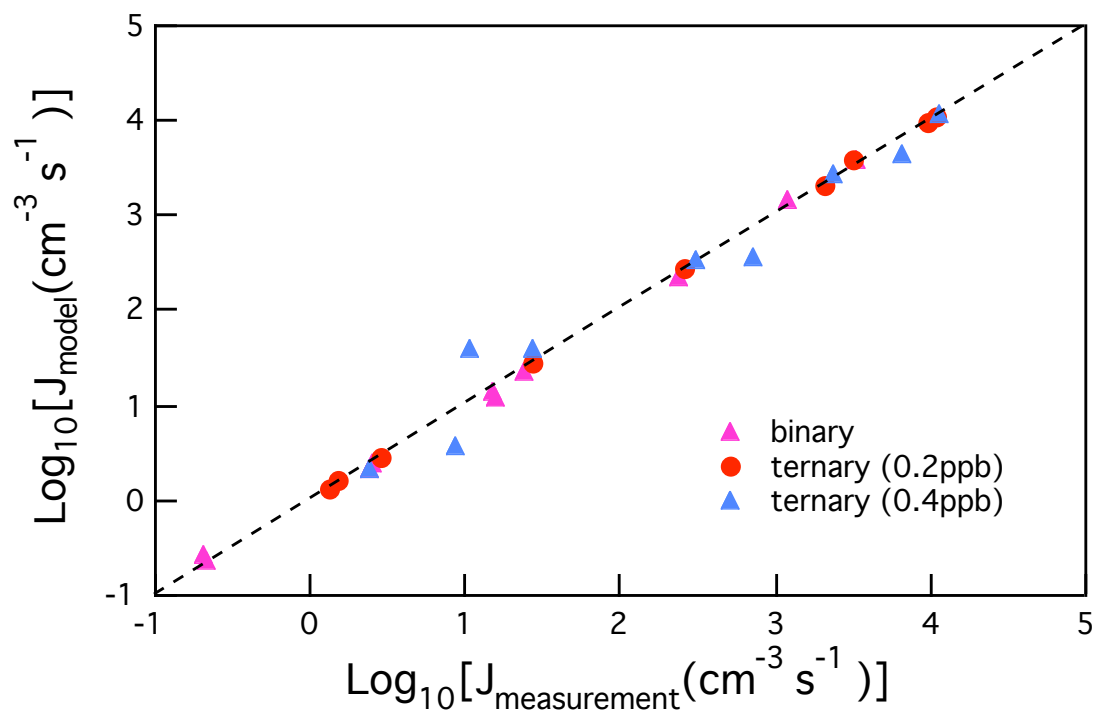# ADDING CONTRIBUTIONS FROM THE BINARY(B) AND TERNARY(T) PATHWAYS

$$J = J_B + J_T$$

$$J_{model}(x,y) =$$

$$10^{-6.58+9.17x} + 10^{-3.67+8.12x+1.86y}$$
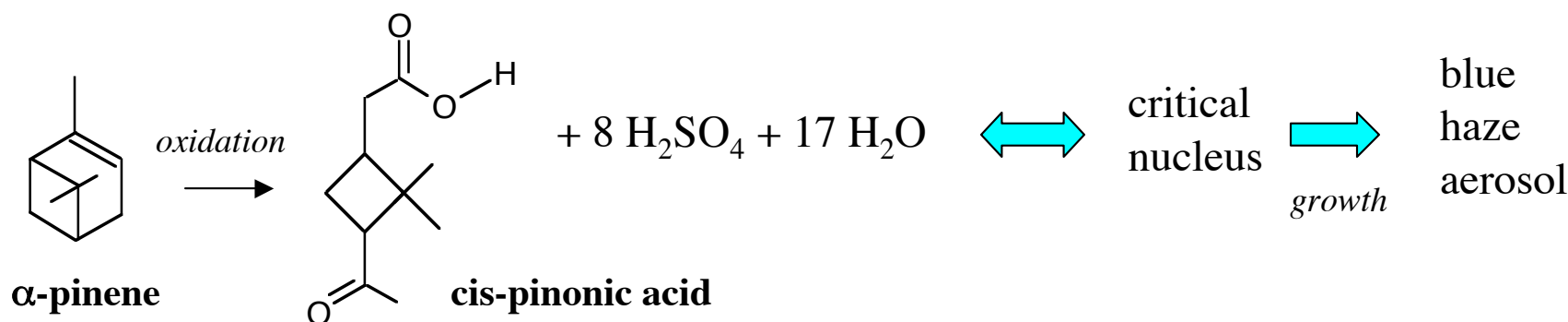
Parameterization of full data set:

$$x = Log_{10}[H_2SO_4, molecules\ cm^{-3}] - 9$$
$$y = Log_{10}[Organic, ppb]$$

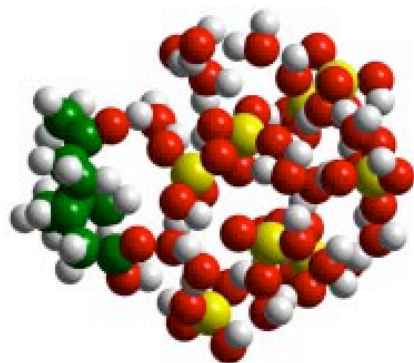Proposed mechanism (involves both natural and anthropogenic precursors):

α-pinene → (oxidation) → **cis-pinonic acid**

$+ 8\ H_2SO_4 + 17\ H_2O$ ⟺ critical nucleus → (growth) → blue haze aerosol

CRITICAL NUCLEUS STRUCTURE FROM MOLECULAR DYNAMICS [2]

1.7 nm

MD simulation of the CPA/ H_2SO_4/H_2O nucleus

Nucleus shows clear separation into hydrophobic and hydrophilic parts connected by hydrogen bonds.

Interpretation: CPA leads to stabilization of the sulfuric acid/water complex and enhancement of nucleation rate over the binary rate.

[2] J. Zhao et al. J. Phys. Chem A113, 680 (2009)
[3] R. Zhang et al. submitted.

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